

# Low-Temperature Emission Control to Enable Fuel-Efficient Engine Commercialization

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**Project ID: ace085**

# Acknowledgments



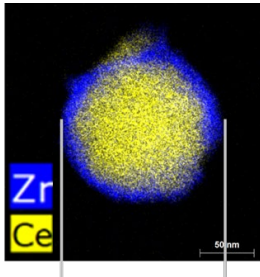
- **Funding & guidance from DOE VTO Program Managers:**
  - Ken Howden, Gurpreet Singh, Mike Weismiller



- **Contributions from the ORNL Team:**
  - Michelle Kidder, Pranaw Kunal, and Michael Lance



- **Collaboration with University At Buffalo:**
  - Judy Liu, Junjie Chen, Prof. Eleni Kyriakidou



- **Access to instrumentation at ORNL:**
  - Micrographs and elemental maps captured using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities

# Project Overview

## Timeline

- Year 1 of 3-year program
  - Project start date:** FY2019
  - Project end date:** FY2021
- Builds on previous R&D in FY16-FY18

## Budget

- FY19: \$500k (Task 1\*)

\*Task 1: Low Temperature Emissions Control Catalysis Research

Part of large ORNL project  
“Controlling Emissions from High Efficiency Combustion Systems”  
(2018 VTO AOP Lab Call)

## Barriers Addressed

U.S. DRIVE Advanced Combustion & Emission Control 2018 Roadmap  
Barriers & Targets:

- Addressing emission compliance barrier to market for advanced fuel-efficient engine technologies, such as 90% conversion of NO<sub>x</sub>, CO and HC at 150°C
- Efficiency, durability, sulfur tolerance of aftertreatment systems

## Collaborators & Partners

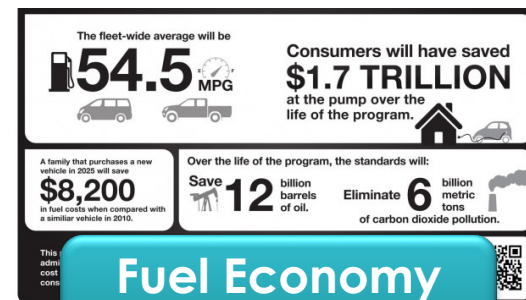
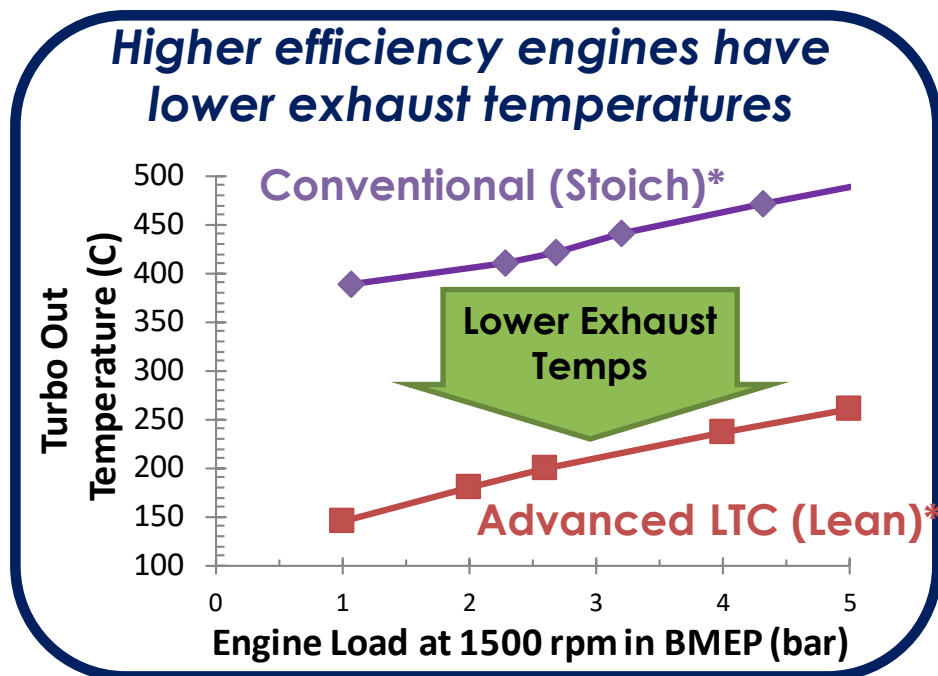
- US DRIVE Advanced Combustion and Emission Control Tech Team
- University at Buffalo (SUNY)

# Objectives and Relevance

Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150°C) to meet emission regulations

Goal: 90% Conversion at 150°C

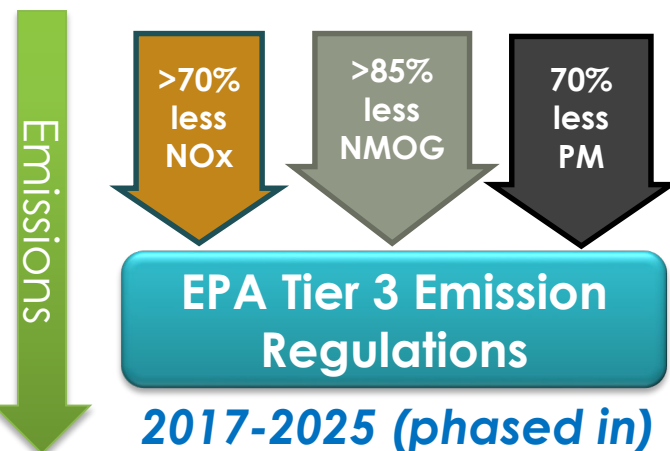
- Greater efficiency lowers exhaust temperature
- Catalysis is challenging at low temperatures
- Emissions standards getting more stringent



**Fuel Economy Standards**

**54.5 mpg CAFE by 2025**

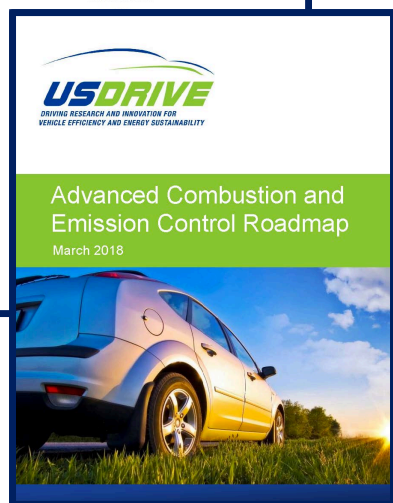
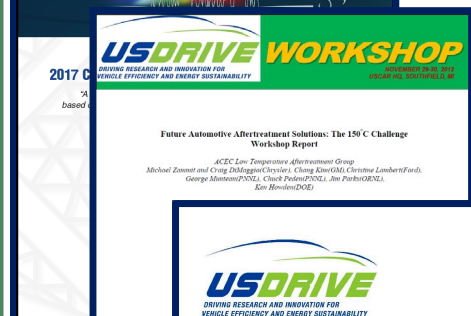
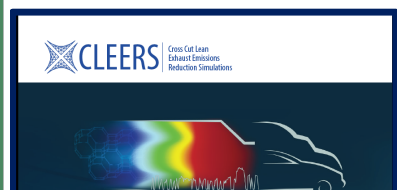
Fuel Economy



\* **"Conventional"**: modern state-of-the-art GDI Turbocharged (stoichiometric)

\* **"Advanced LTC"**: advanced lean-burn Low Temperature Combustion (LTC) engine

# Relevance: Guiding Documents Define Industry Needs



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## Identified Needs Addressed:

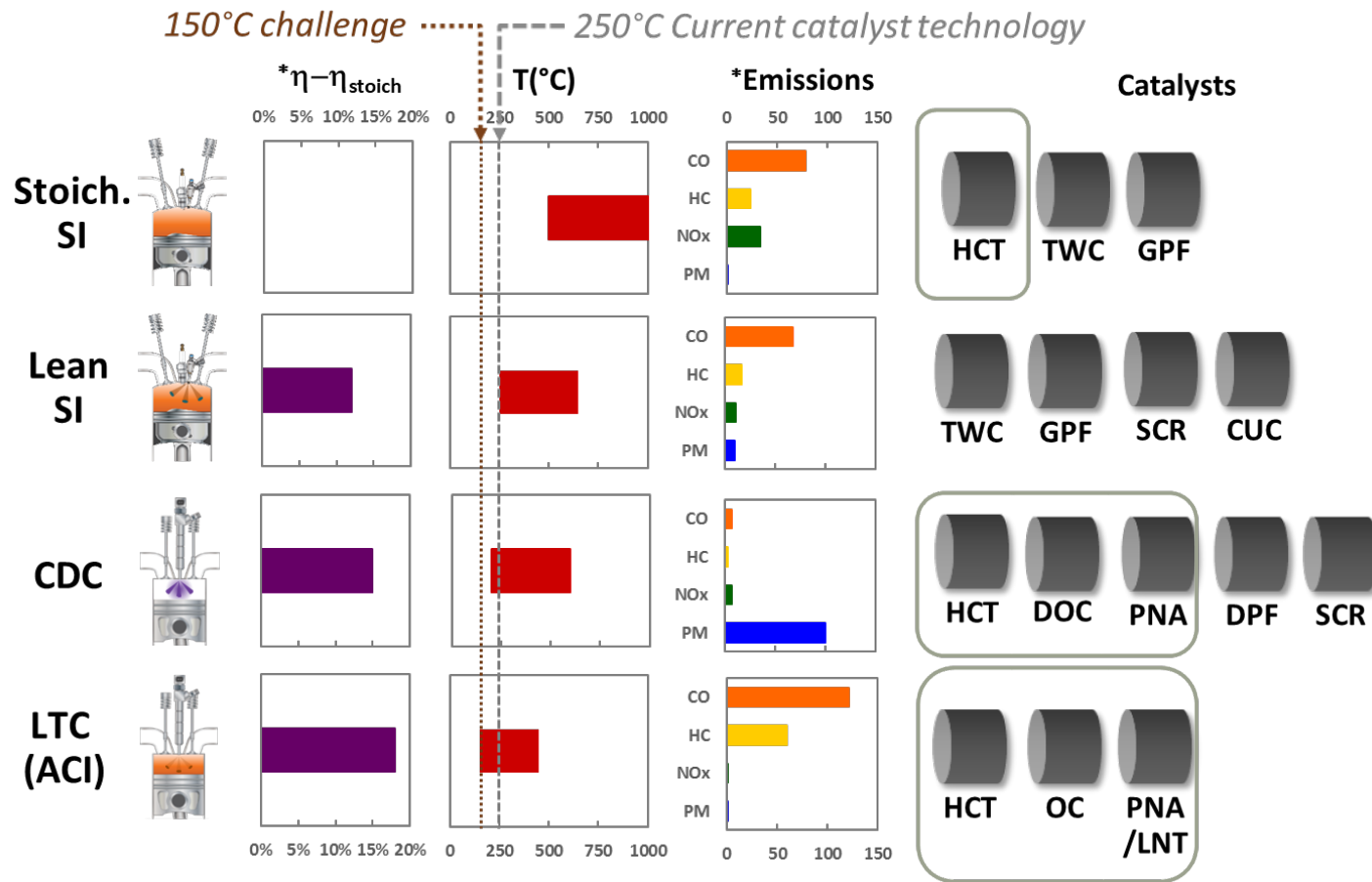
- Lower temperature CO and HC oxidation
- Low temperature NOx reduction
- Cold start emission trapping technologies
  - Especially passive NOx adsorbers
- Reduced PGM
- Better durability
- Promote innovative catalytic solutions via partnering with DOE BES programs

Low Temperature Combustion (LTC)

Dilute Gasoline Combustion

Clean Diesel Combustion (CDC)

# Approach: Lean low-temperature exhaust creates emissions challenges that must be addressed



**Low Temperature Emissions Control**  
Discover new low T catalysts & traps

**CLEERS**  
Model new trap materials

**Lean Gasoline Emissions Control**  
Develop emissions pathway for lean gasoline engines to meet emissions

**Chemistry and Control of Cold Start Emissions**  
exhaust chemistry impact on functionality

**TWC:** three-way catalyst  
**HCT:** hydrocarbon trap  
**PF:** particulate filter

**SCR:** selective catalytic NOx reduction  
**CUC:** CO/HC clean-up catalyst  
**OC:** oxidation catalyst

**PNA:** passive NOx adsorber  
**LNT:** lean NOx trap  
\* — semi-quantitative representation



# Employ low temperature protocols to evaluate catalysts

- Project employs US DRIVE Advanced Combustion and Emission Control Team Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation
- Full protocol at: [www.CLEERS.org](http://www.CLEERS.org)

## LTC-D: Low Temp. Combustion Diesel

Total HC<sub>1</sub>: 3000 ppm

C<sub>2</sub>H<sub>4</sub>: 500 ppm

C<sub>3</sub>H<sub>6</sub>: 300 ppm

C<sub>3</sub>H<sub>8</sub>: 100 ppm

\*C<sub>12</sub>H<sub>26</sub>: **2100 ppm**

CO: 2000 ppm

NO: 100 ppm

H<sub>2</sub>: 400 ppm

H<sub>2</sub>O: 6 %

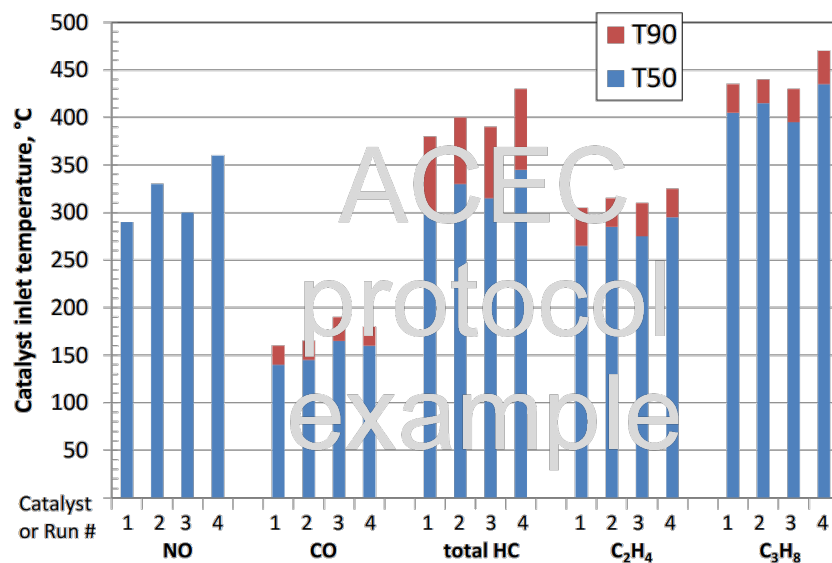
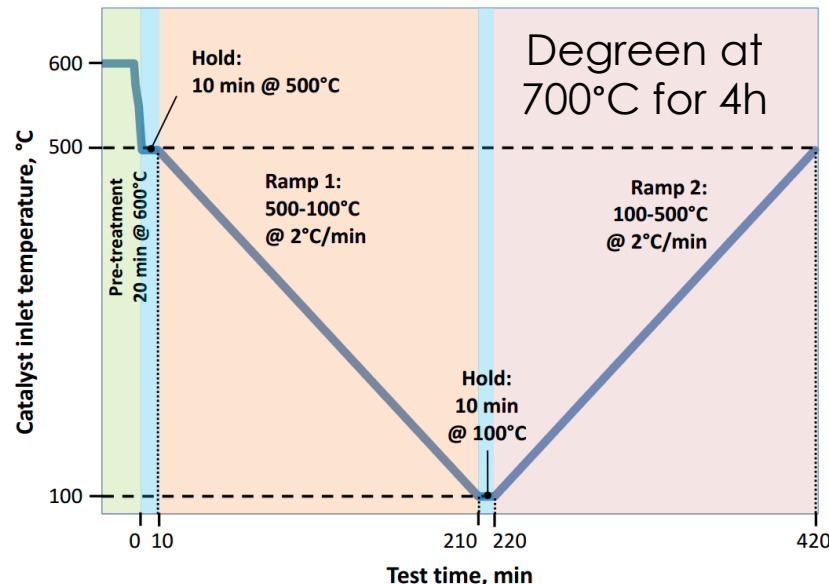
CO<sub>2</sub>: 6 %

O<sub>2</sub>: 12 %

Balance N<sub>2</sub>

## Powder Catalyst Requirements

- Reactor ID 3-13 mm
- Catalyst particle size ≤ 0.25 mm
- Catalyst bed L/D ≥ 1
- Space velocity
  - 200-400 L/g-hr
  - For 0.1 g, flow 333-666 sccm



# Collaborations

- **Academia**

- **University at Buffalo (SUNY):** Prof. Eleni Kyriakidou, Judy Liu, Junjie Chen
  - Catalyst synthesis, characterization, and evaluation
- **Harvard University:** Wyss Institute for Biologically Inspired Engineering, Prof. Joanna Aizenberg
  - Evaluation of new types structured/stable catalysts (PGM supported on metal oxides)
- **Karlsruhe Institute of Technology:** joint paper on oxidation catalysts with Olaf Deutschmann

- **Industry**

- **USCAR/USDRIVE Low Temperature Aftertreatment (LTAT) working group**
  - low temperature evaluation protocols
- **Johnson Matthey:** Industry input from Haiying Chen; partner on DOE project Sharan Sethuraman

- **DOE Basic Energy Science researchers**

- Sheng Dai and Ashi Savara (ORNL), Center for Nanophase Materials Science
  - Catalysts synthesis and characterization

- **Other DOE funded projects**

- **CLEERS:** Dissemination of data; presentation at CLEERS workshops
- **PNNL:** bi-monthly teleconferences established to share data on VTO projects
- **University of Houston-led project with University of Virginia, Johnson Matthey, Southwest Research Institute**
  - Project focusing on low temperature catalysis



# Milestones of 3-year project

- FY19 Milestones: **on track**

- Determine ion-exchange/nanoparticle distribution in HCT/PNA

- FY20 Milestones: **on track**

- Determine which multifunctional configuration yields the highest activity while simulating cold start heating rates using the top performing HC Trap/PNA + DOC

- FY21 Milestones: **on track**

- Demonstrate 90% conversion of criteria pollutants CO, HC, and NO<sub>x</sub> at 150°C on hydrothermally-aged catalysts

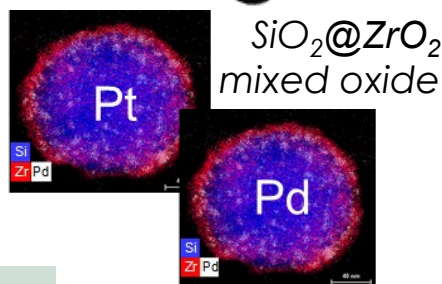
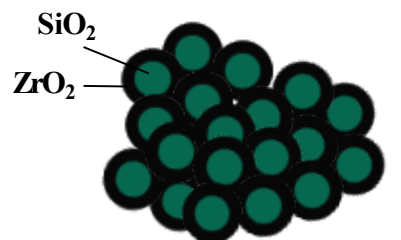
# Technical Accomplishments

- Oxidation catalysts
- Trap/Adsorber Materials
  - Hydrocarbon trap
  - Passive NO<sub>x</sub> adsorbers
- Combined systems



# Results are building on promising $\text{SiO}_2@\text{ZrO}_2$ core@shell support for Pt and Pd catalysts

- PGM supported on a shell of  $\text{ZrO}_2$  around a core of  $\text{SiO}_2$  ( $\text{SiO}_2@\text{ZrO}_2$ )
- Exceptional low temperature activity observed with Pt+Pd physical mixture
  - Bed loading: 1.8% Pt and 1.0% Pd
  - Initially, aged at 800 °C for 10h



Conditions during 2°C ramp

total HC<sub>1</sub>: 3000 ppm

C<sub>2</sub>H<sub>4</sub>: 500 ppm

C<sub>3</sub>H<sub>6</sub>: 300 ppm

C<sub>3</sub>H<sub>8</sub>: 100 ppm

C<sub>10</sub>H<sub>22</sub>: 2100 ppm

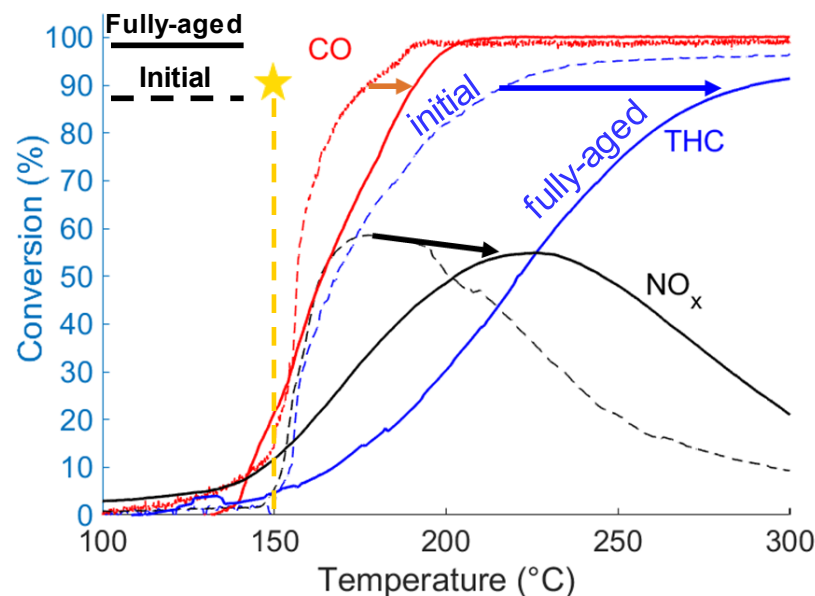
CO: 2000 ppm

NO: 100 ppm

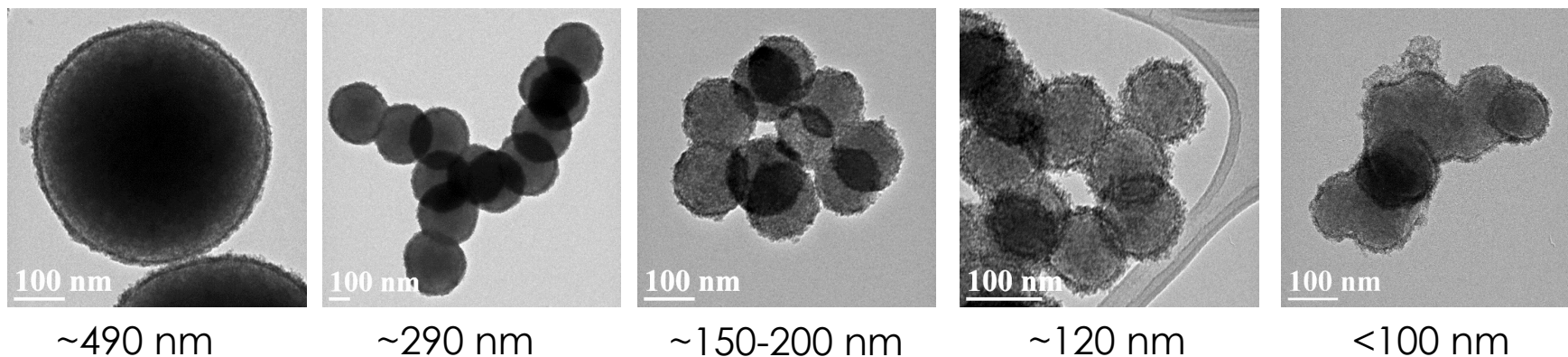
Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>

*Protocol aging: reaction conditions at 800°C for 50h, 5 ppm SO<sub>2</sub> @ 300°C 5 h*

- Investigating improved durability of Pt and Pd on novel supports has been the focus of project
- Improving initial dispersion, and maintaining small Pt + Pd particle sizes throughout aging protocol



# Varying diameter of $\text{SiO}_2@\text{ZrO}_2$ initiated with goal of creating surface that is less prone to Pt /Pd sintering



- Loading Pd on smaller  $\text{SiO}_2@\text{ZrO}_2$  spheres led to **higher** dispersion
  - Higher surface area may prevent Pd agglomeration
- Initially focusing on the 150-200 nm supports with Pd, Pt, and combinations
  - Evaluation of all supports forthcoming

$\text{SiO}_2$ size	> 450 nm	150-200 nm
Si@Zr BET SA	147 m <sup>2</sup> /g	376 m <sup>2</sup> /g
Si@Zr BJH PV	0.14 cm <sup>3</sup> /g	0.33 cm <sup>3</sup> /g
Pd dispersion*	3.9 %	24.1 %
Avg. Pd size*	28.8 nm	4.6 nm

\* - based on CO chemisorption values and spherical particles size assumption

# Combinations with Pd and Pt continue to show the best reactivity, but 150 °C goal is still elusive

- Supports continue to show good initial THC reactivity, but not reaching 90% conversion until ~250 °C
- Other oxidation catalysts are under consideration

*Conditions during 2°C ramp*

*total HC<sub>1</sub>: 3000 ppm*

*C<sub>2</sub>H<sub>4</sub>: 500 ppm*

*C<sub>3</sub>H<sub>6</sub>: 300 ppm*

*C<sub>3</sub>H<sub>8</sub>: 100 ppm*

*C<sub>10</sub>H<sub>22</sub>: 2100 ppm*

*CO: 2000 ppm*

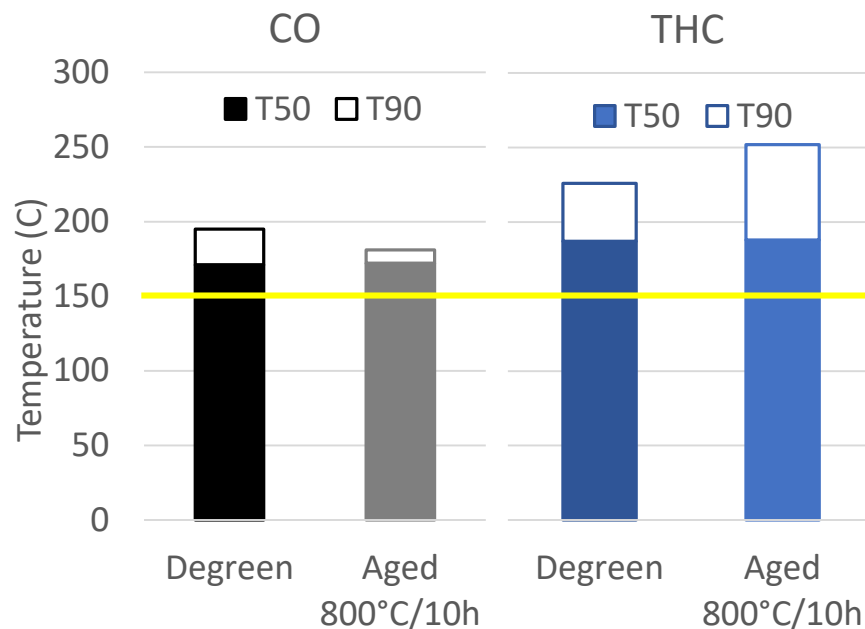
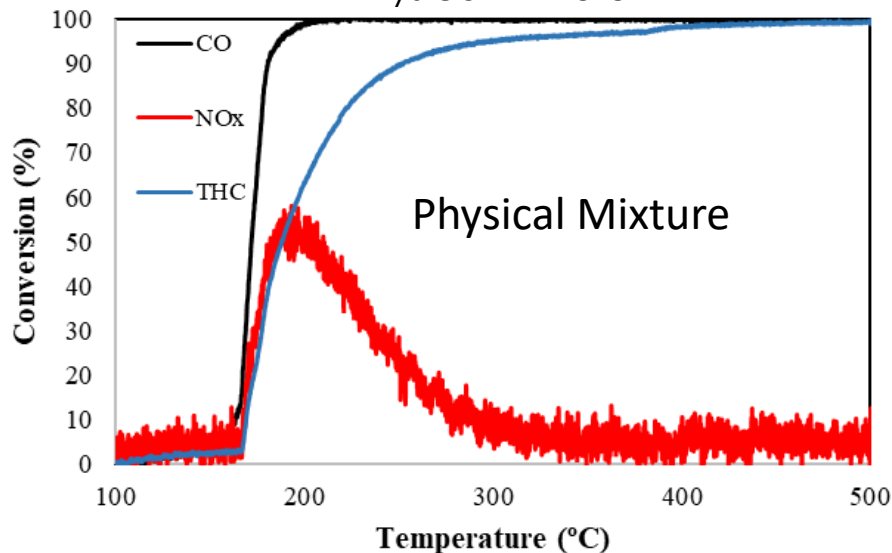
*NO: 100 ppm*

*Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>*

**Hydrothermally aged at 800 °C for 10h**

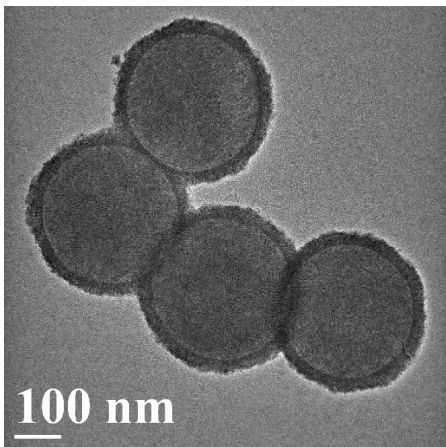
1% Pd/SiO<sub>2</sub>@ZrO<sub>2</sub> + 1.8% Pt/SiO<sub>2</sub>@ZrO<sub>2</sub>

Physical Mixture

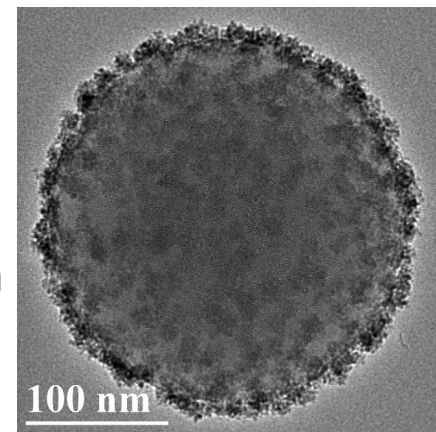




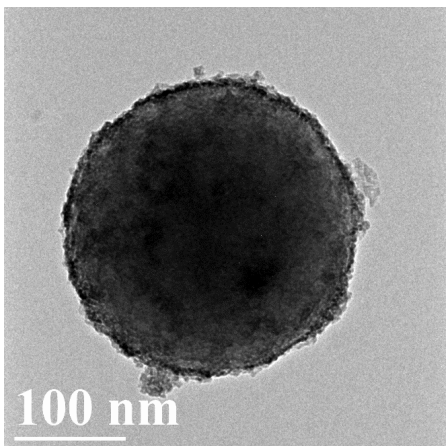
# Other supports to be evaluated



- $\text{SiO}_2@ZrO_2$  core@shell
  - Average diameter: 340 nm

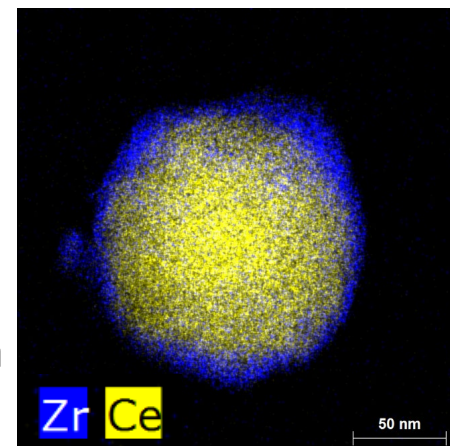


- $\text{SiO}_2@CeO_2$  core@shell
  - Average diameter: 260 nm



- $\text{SiO}_2@CeO_2-ZrO_2$  core@shell
  - Average diameter: 260 nm

- $CeO_2@ZrO_2$  core@shell
  - Average diameter: 150 nm





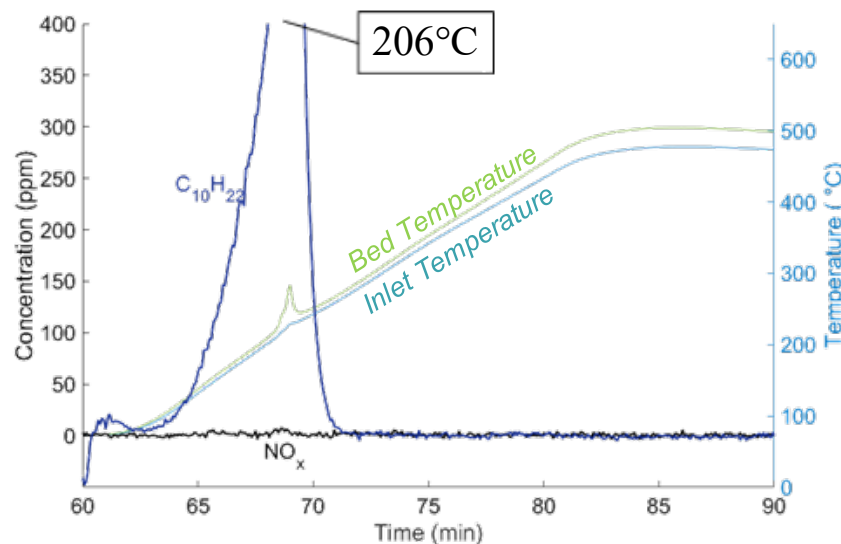
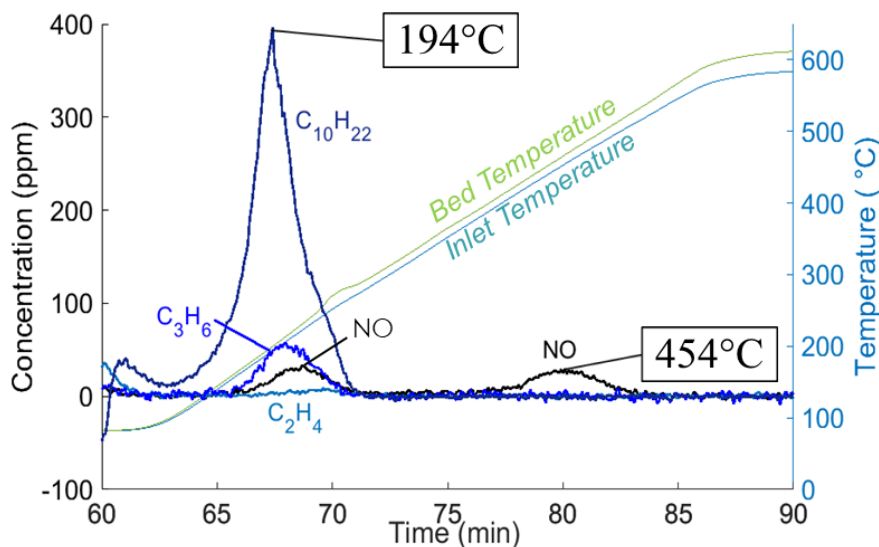
# Technical Accomplishments

- Oxidation catalysts
- Trap/Adsorber Materials
  - Hydrocarbon trap
  - Passive NO<sub>x</sub> adsorbers
- Combined systems



Pd/ZSM-5 initially is a combination HC Trap and Passive NO<sub>x</sub> Adsorber, but loses NO<sub>x</sub> functionality with aging

### Pd/ZSM-5 only: HC/NO release following 30 min storage



- Pd/ZSM-5 shows favorable release temperatures for pairing with an active DOC catalyst
- Release of NO across two peak temperatures
- Most functionality of Pd/ZSM-5 lost after aging;  
→ However, decane is still trapped very effectively
- Indicates ion-exchanged Pd does not exist after aging  
– shown in literature to be essential for NO adsorption\*

Conditions during 30 min storage step at 100°C

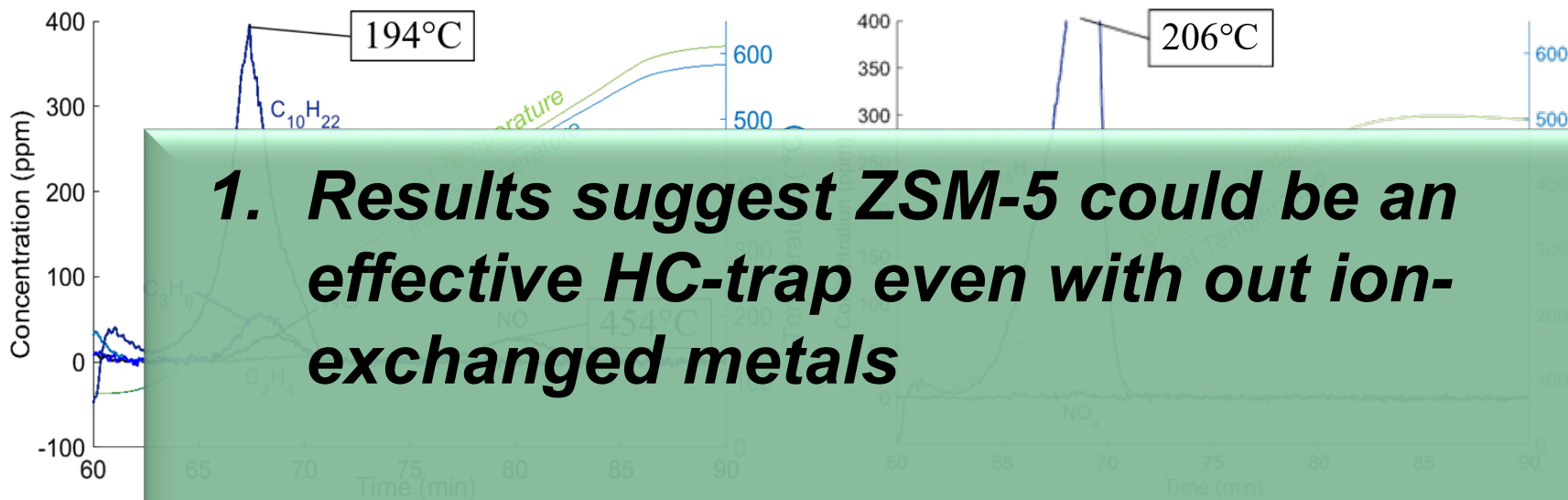
total HC<sub>1</sub>: 3000 ppm  
C<sub>2</sub>H<sub>4</sub>: 500 ppm  
C<sub>3</sub>H<sub>6</sub>: 300 ppm  
C<sub>3</sub>H<sub>8</sub>: 100 ppm  
C<sub>10</sub>H<sub>22</sub>: 2100 ppm

CO: 2000 ppm  
NO: 100 ppm

Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>

Pd/ZSM-5 initially is a combination HC Trap and Passive NO<sub>x</sub> Adsorber, but loses NO<sub>x</sub> functionality with aging

**Pd/ZSM-5 only:** HC/NO release following 30 min storage



**1. Results suggest ZSM-5 could be an effective HC-trap even with out ion-exchanged metals**

**2. More durable zeolite needed to maintain NO adsorption functionality after 800°C**

- Pd/ZSM-5 shows an active DOC catalyst
- Release of NO across two peak temperatures
- Most functionality of Pd/ZSM-5 lost after aging;  
→ However, decane is still trapped very effectively
- Indicates ion-exchanged Pd does not exist after aging  
— shown in literature to be essential for NO adsorption\*

$C_3H_6$ : 300 ppm  
 $C_3H_8$ : 100 ppm  
 $C_{10}H_{22}$ : 2100 ppm  
 CO: 2000 ppm  
 NO: 100 ppm  
 Also  $H_2$ ,  $O_2$ ,  $H_2O$  and  $CO_2$

# Unexchanged ZSM-5 shows considerable HC storage; mostly heavy hydrocarbons

- Evaluation:
  - 30 min at 100°C → 20°C/min ramp to 600°C → hold 4h
- FID measurement indicates 2.5-3.0 mmols/g<sub>cat</sub>
  - Measured during desorption
  - C<sub>10</sub>H<sub>22</sub> comprises 88-93% of THC adsorption

*LTC-D oxidation protocol  
conditions during 30 min  
storage step at 100°C*

---

*total HC<sub>1</sub>: 3000 ppm*

*C<sub>2</sub>H<sub>4</sub>: 500 ppm*

*C<sub>3</sub>H<sub>6</sub>: 300 ppm*

*C<sub>3</sub>H<sub>8</sub>: 100 ppm*

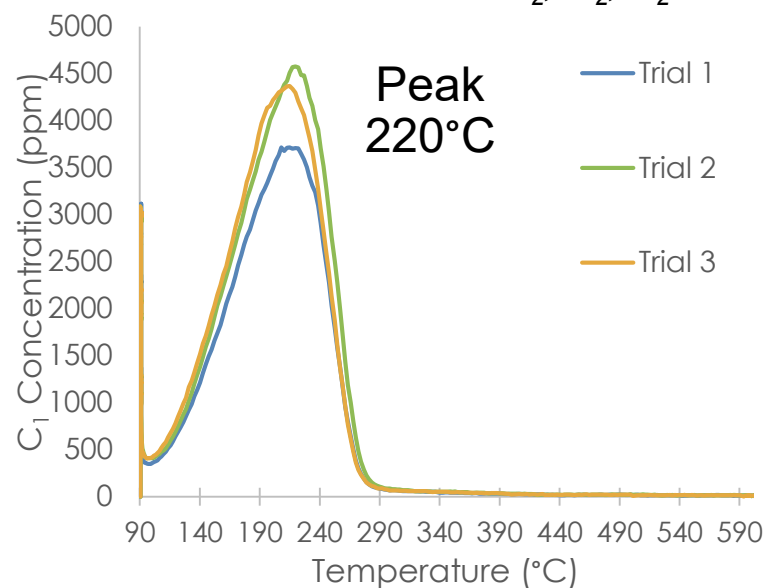
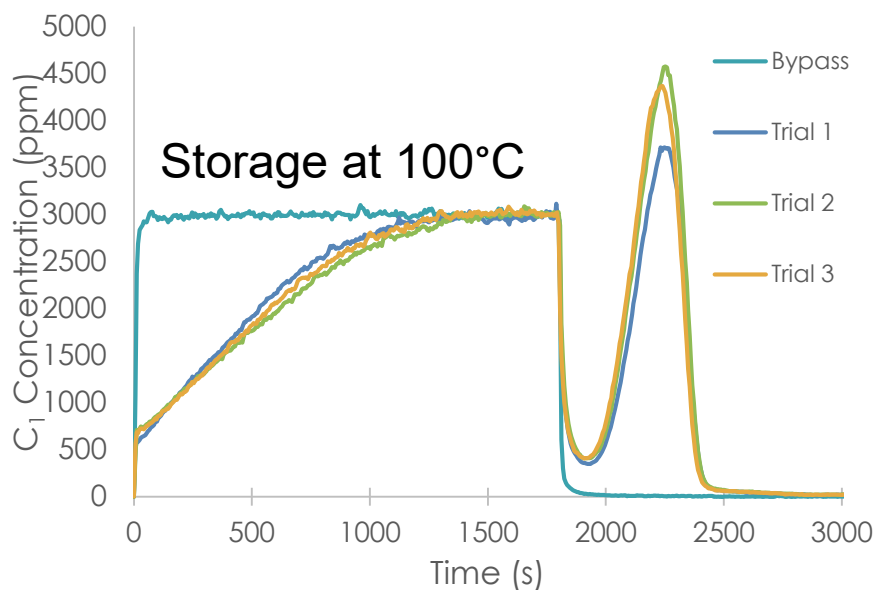
*C<sub>10</sub>H<sub>22</sub>: 2100 ppm*

*CO: 2000 ppm*

*NO: 100 ppm*

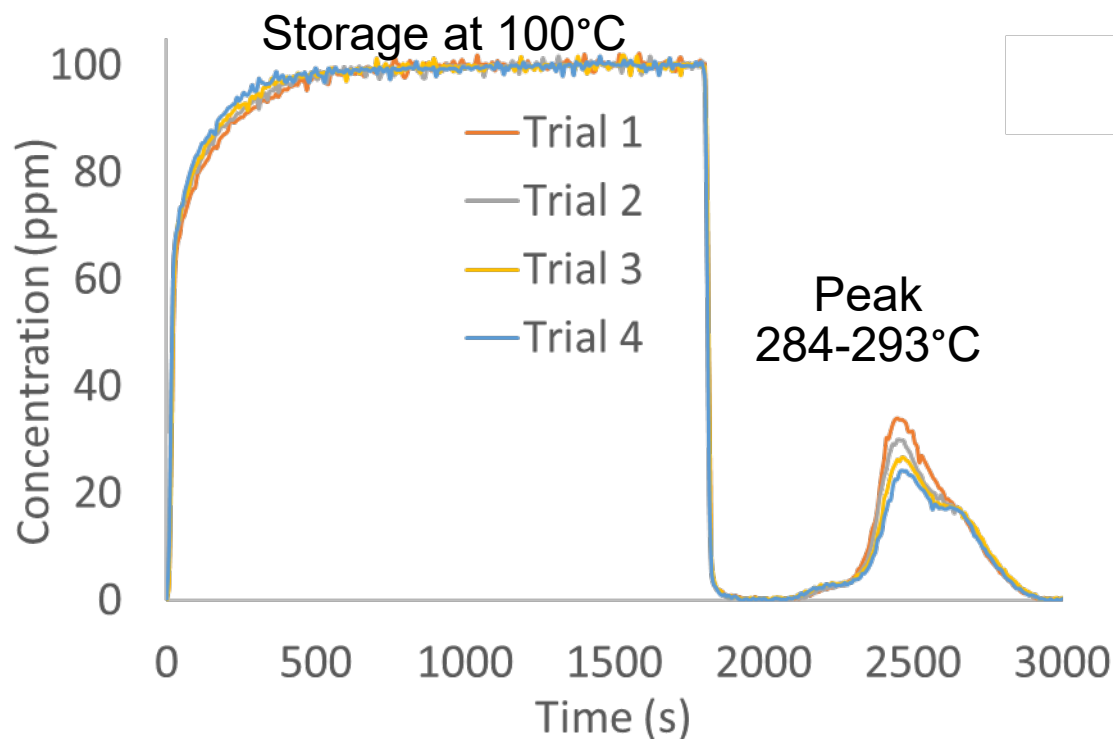
*Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>*

## Total Hydrocarbons: FID



# Pd/SSZ-13 capable of storing significant NO under US-DRIVE protocol relevant conditions

- Synthesized 1% ion-exchanged Pd/SSZ-13 using commercially available SSZ-13 zeolite
- Evaluation:
  - 30 min at 100°C → 20°C/min ramp to 600°C → hold 1 h



*LTC-D oxidation protocol conditions during 30 min storage step at 100°C*

total HC<sub>1</sub>: 3000 ppm

C<sub>2</sub>H<sub>4</sub>: 500 ppm

C<sub>3</sub>H<sub>6</sub>: 300 ppm

C<sub>3</sub>H<sub>8</sub>: 100 ppm

C<sub>10</sub>H<sub>22</sub>: 2100 ppm

CO: 2000 ppm

NO: 100 ppm

Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>

- NO: Pd decreases from 0.22 to 0.18 mol: mol
- Decreasing NO adsorption/desorption between trials
  1. Incomplete NO removal?
  2. Loss of Pd ion-exchange sites

# Extending high temperature regen from 1h to 4h stabilizes NO storage capacity but losses still apparent

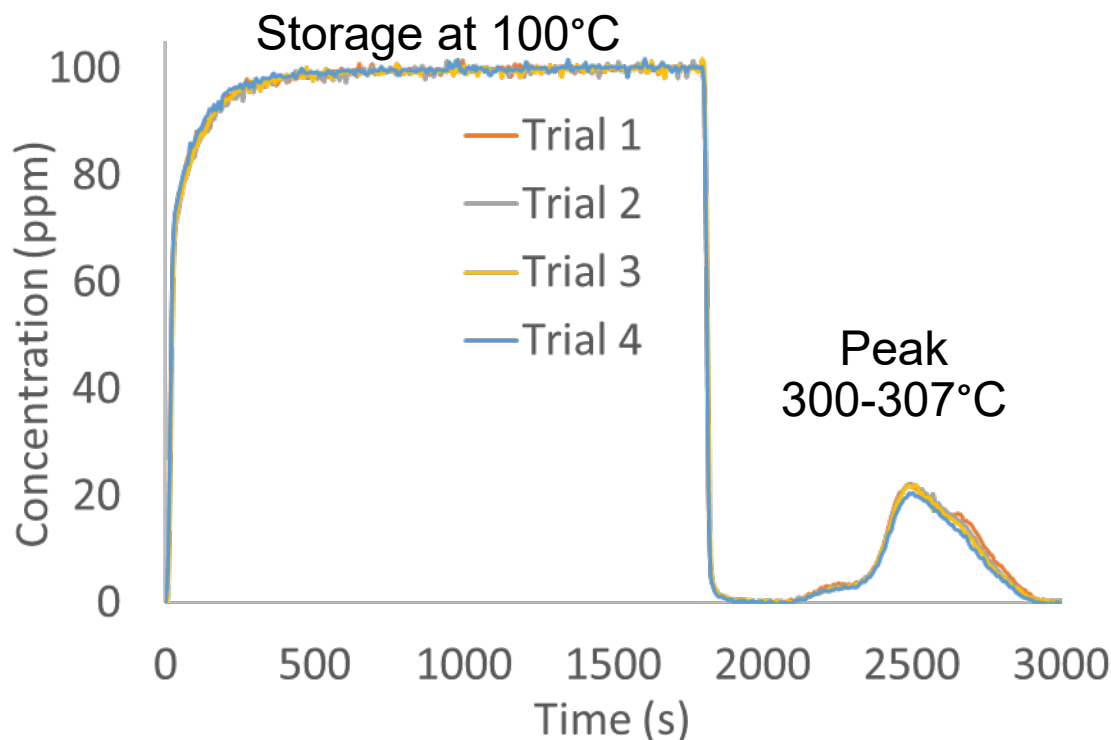
- Synthesized 1% ion-exchanged Pd/SSZ-13 using commercially available SSZ-13 zeolite
- Evaluation:
  - 30 min at 100°C → 20°C/min ramp to 600°C → hold 4h

*LTC-D oxidation protocol conditions during 30 min storage step at 100°C*

---

total HC <sub>1</sub> :	3000 ppm
C <sub>2</sub> H <sub>4</sub> :	500 ppm
C <sub>3</sub> H <sub>6</sub> :	300 ppm
C <sub>3</sub> H <sub>8</sub> :	100 ppm
C <sub>10</sub> H <sub>22</sub> :	2100 ppm
CO:	2000 ppm
NO:	100 ppm

Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>



- NO: Pd stabilizes around 0.16 mol: mol
  - Lower than originally measured, 0.22-0.18
- Prefer higher uptake and Pd utilization



# Aging Pd/SSZ-13 (US-DRIVE protocol) results in improved NO<sub>x</sub> uptake, suggesting incomplete initial ion-exchange

- Hydrothermal aging at 800 °C for 25h
- Evaluation:
  - 30 min at 100°C → 20°C/min ramp to 600°C → hold 4h

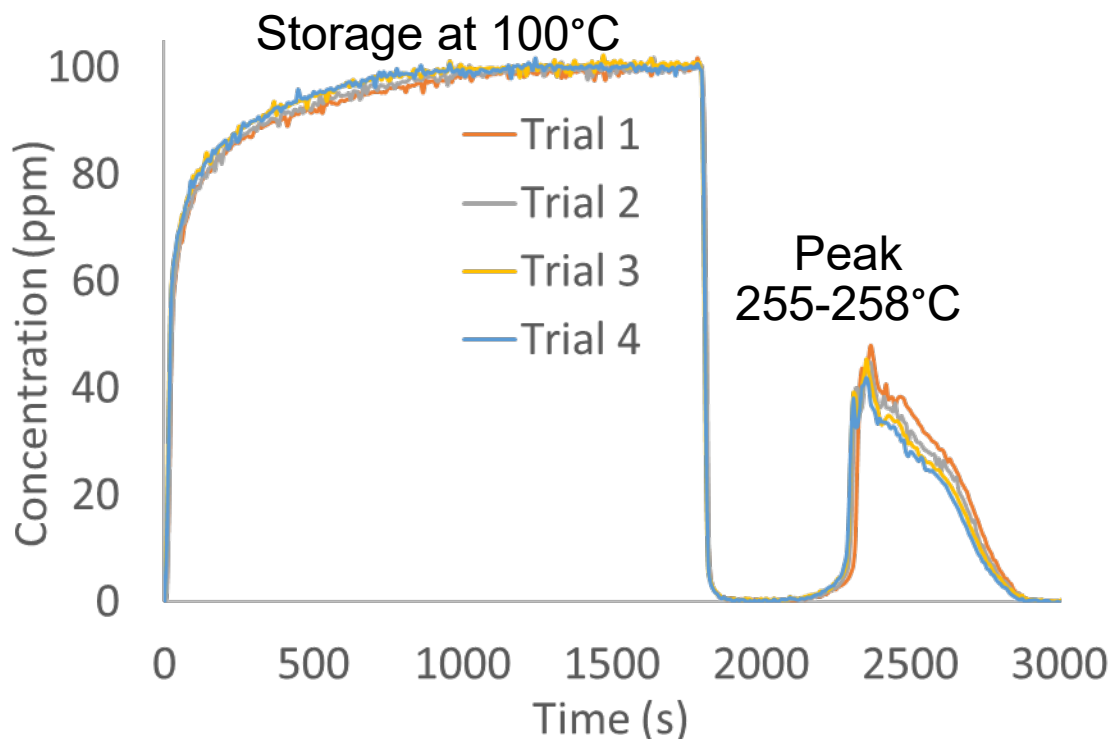
*LTC-D oxidation protocol conditions during 30 min storage step at 100°C*

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total HC <sub>1</sub> :	3000 ppm
C <sub>2</sub> H <sub>4</sub> :	500 ppm
C <sub>3</sub> H <sub>6</sub> :	300 ppm
C <sub>3</sub> H <sub>8</sub> :	100 ppm
C <sub>10</sub> H <sub>22</sub> :	2100 ppm
CO:	2000 ppm
NO:	100 ppm

Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>

After aging for 25h at 800°C

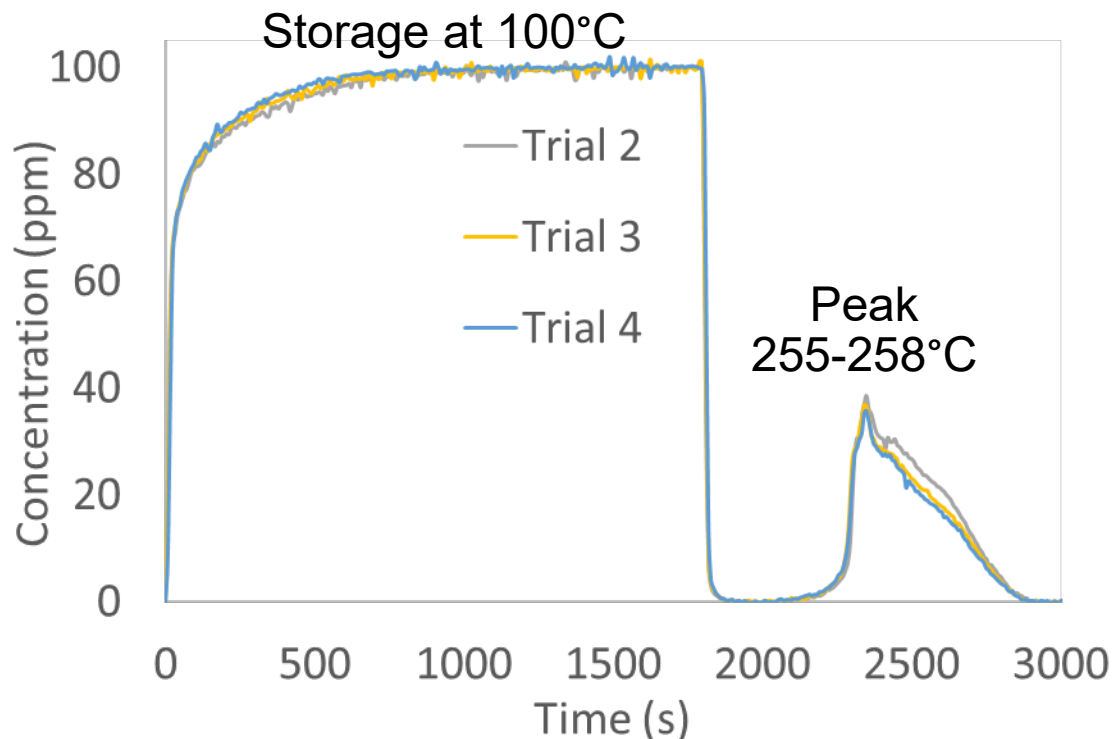


- NO: Pd increases to 0.3 mol: mol
  - Up from 0.16 mol: mol
- Still observing decreased adsorption with each trial
  - 0.32 → 0.30 → 0.28 → 0.27

# Aging Pd/SSZ-13 (US-DRIVE protocol) results in improved NO<sub>x</sub> uptake, suggesting incomplete initial ion-exchange

- Hydrothermal aging at 800 °C for 50h
- Evaluation:
  - 30 min at 100°C → 20°C/min ramp to 600°C → hold 4h

After aging for 50h at 800°C



*LTC-D oxidation protocol  
conditions during 30 min  
storage step at 100°C*

*total HC<sub>1</sub>: 3000 ppm*

*C<sub>2</sub>H<sub>4</sub>: 500 ppm*

*C<sub>3</sub>H<sub>6</sub>: 300 ppm*

*C<sub>3</sub>H<sub>8</sub>: 100 ppm*

*C<sub>10</sub>H<sub>22</sub>: 2100 ppm*

*CO: 2000 ppm*

*NO: 100 ppm*

*Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>*

- With continued aging and evaluation NO:Pd continues to decrease
  - 0.24 → 0.23 → 0.22 mol:mol
- Suggests loss of Pd ion-exchange sites
  - Goal is to quantify

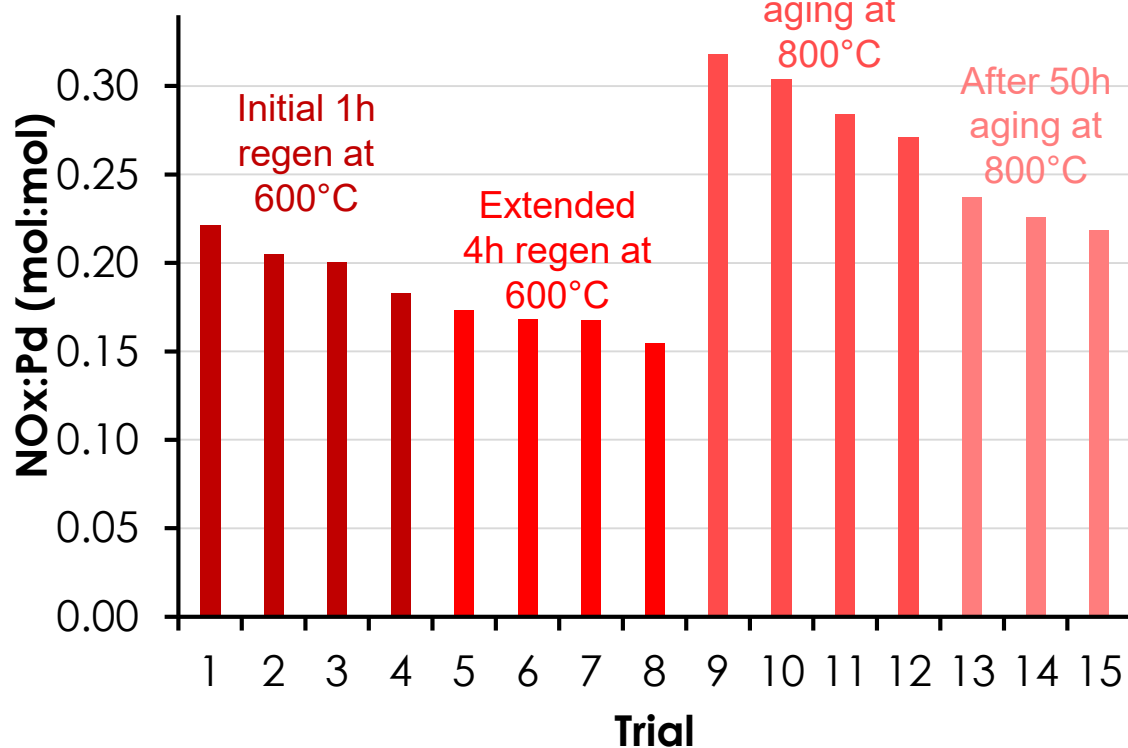
# Tracking NO uptake shows steady decrease

- Evaluation:

- 30 min at 100°C → 20°C/min ramp to 600°C → hold 4h

*LTC-D oxidation protocol conditions during 30 min storage step at 100°C*

NO<sub>x</sub>:Pd (mol/mol)



total HC<sub>1</sub>: 3000 ppm

C<sub>2</sub>H<sub>4</sub>: 500 ppm

C<sub>3</sub>H<sub>6</sub>: 300 ppm

C<sub>3</sub>H<sub>8</sub>: 100 ppm

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Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>

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*LTC-D oxidation protocol conditions during 30 min storage step at 100°C*

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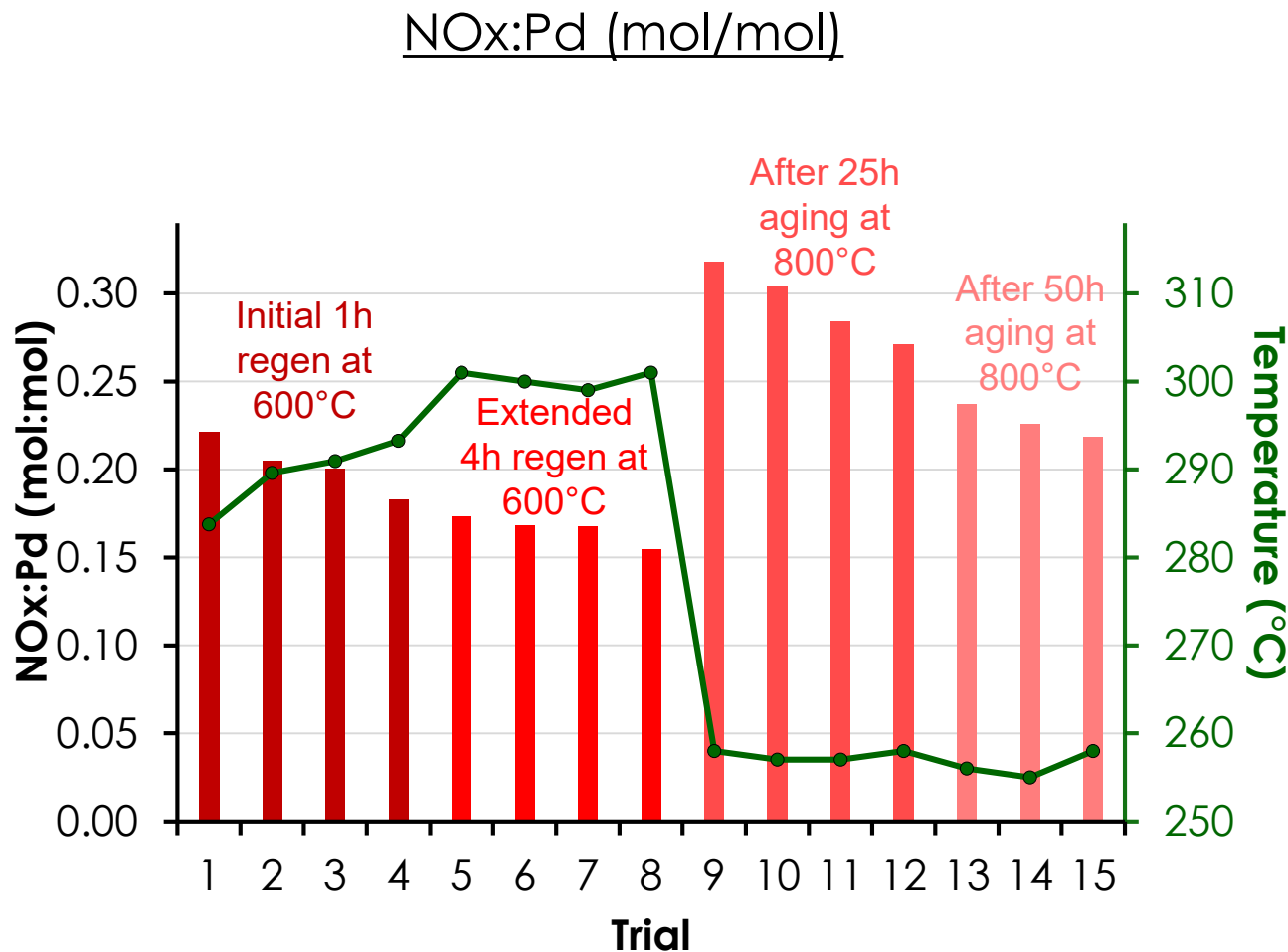
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Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>



# Technical Accomplishments

- Oxidation catalysts
- Trap/Adsorber Materials
  - Hydrocarbon trap
  - Passive NO<sub>x</sub> adsorbers
- Combined systems



# Combining ZSM-5 + Pd/SSZ-13 illustrates stable NO and THC after 4 trials; NO uptake increases

## • Evaluation:

- Degreen at 700°C for 15 h
- 30 min at 100°C → 20°C/min ramp to 600°C → hold 4h
- Mixture of 100mg ZSM-5 + 100mg 1% Pd/SSZ-13
- Overall 200 L/g-h including both catalysts (666 sccm)

*LTC-D oxidation protocol conditions during 30 min storage step at 100°C*

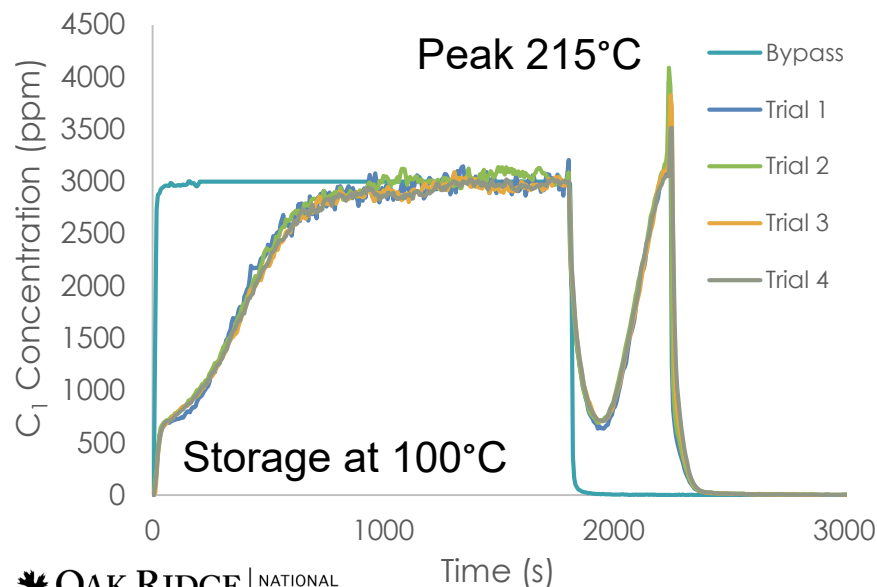
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total HC<sub>1</sub>: 3000 ppm  
 C<sub>2</sub>H<sub>4</sub>: 500 ppm  
 C<sub>3</sub>H<sub>6</sub>: 300 ppm  
 C<sub>3</sub>H<sub>8</sub>: 100 ppm  
 C<sub>10</sub>H<sub>22</sub>: 2100 ppm  
 CO: 2000 ppm  
 NO: 100 ppm  
 Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>

## • HC uptake 2.4-2.6 mmols/g<sub>cat</sub>

- Measured during adsorption

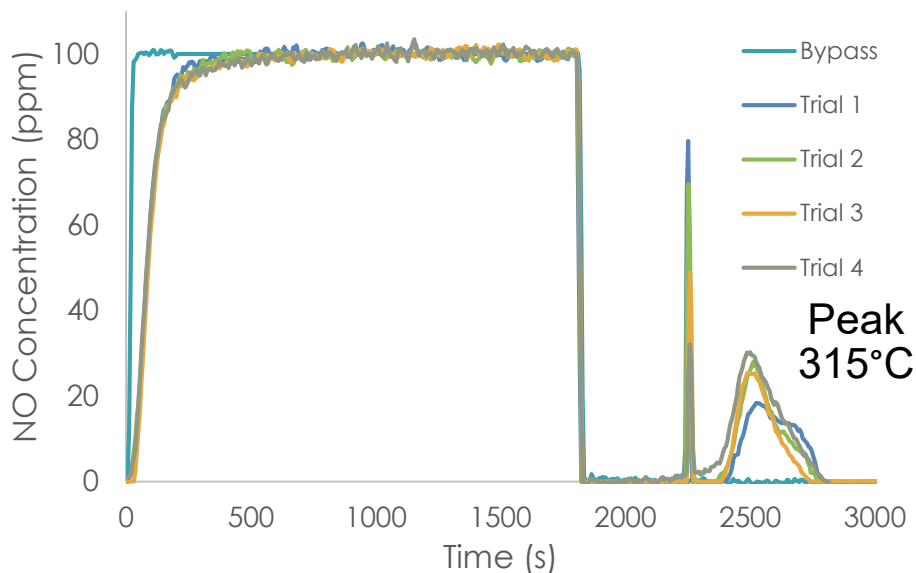
*Total Hydrocarbons: FID*



## • NO: Pd ratio 0.50-0.53 mol:mol

- Measured during adsorption

*Total NOx: chemiluminescence*





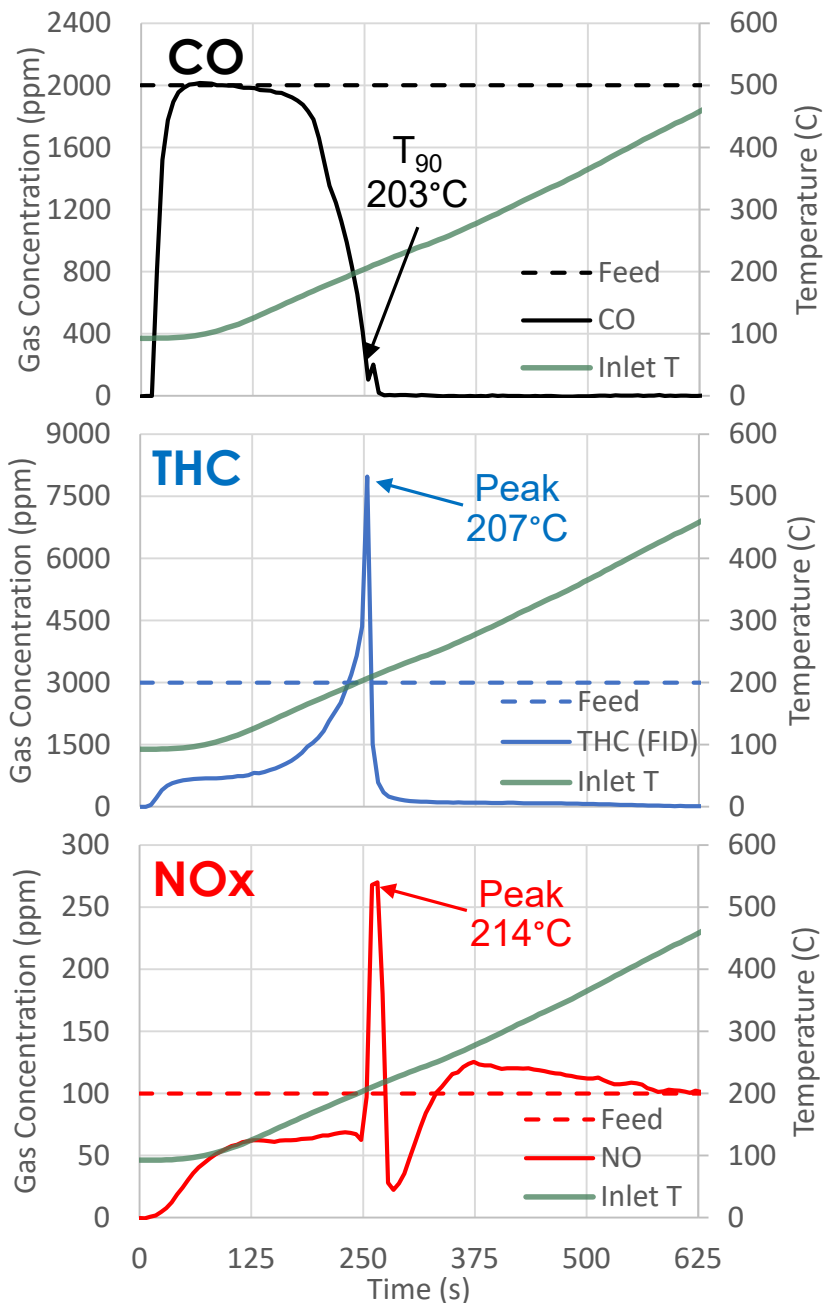
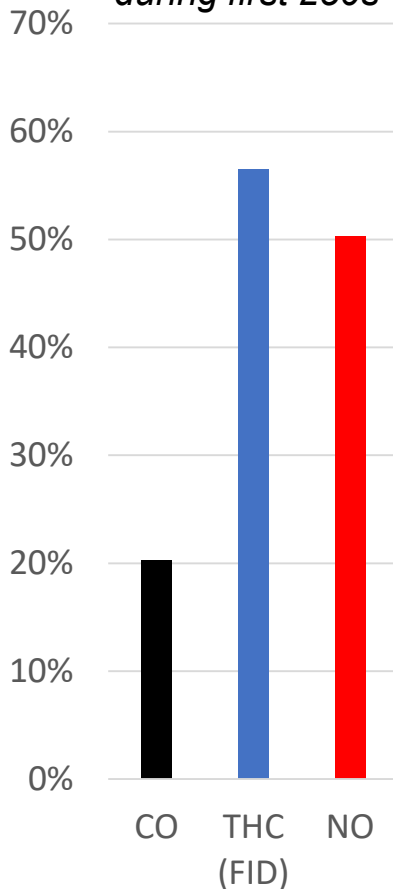
# Adding oxidation catalyst shows overall conversion of >50% for THC and NOx

## • Evaluation:

- Introduce reactants and immediately begin ramp
  - 40°C/min ramp to 620°C
- Physical Mixture of
  - 100 mg ZSM-5
  - 100 mg 1% Pd/SSZ-13
  - 100 mg 0.9% Pt/0.5% Pd/SiO<sub>2</sub>@ZrO<sub>2</sub>
- Overall 133 L/g-h including all three catalysts (666 sccm)
- Release of HCs overwhelms oxidation catalyst
  - Need higher activity or more catalyst
- NO:Pd at 250s = 0.68
  - Based on mols in Pd/SSZ-13

**Degreened 15h/700°C**

*Overall %removal during first 250s\**



\* - Based on Ford study relevant to cold start and time to catalyst lightoff (SAE 2018-01-0938).

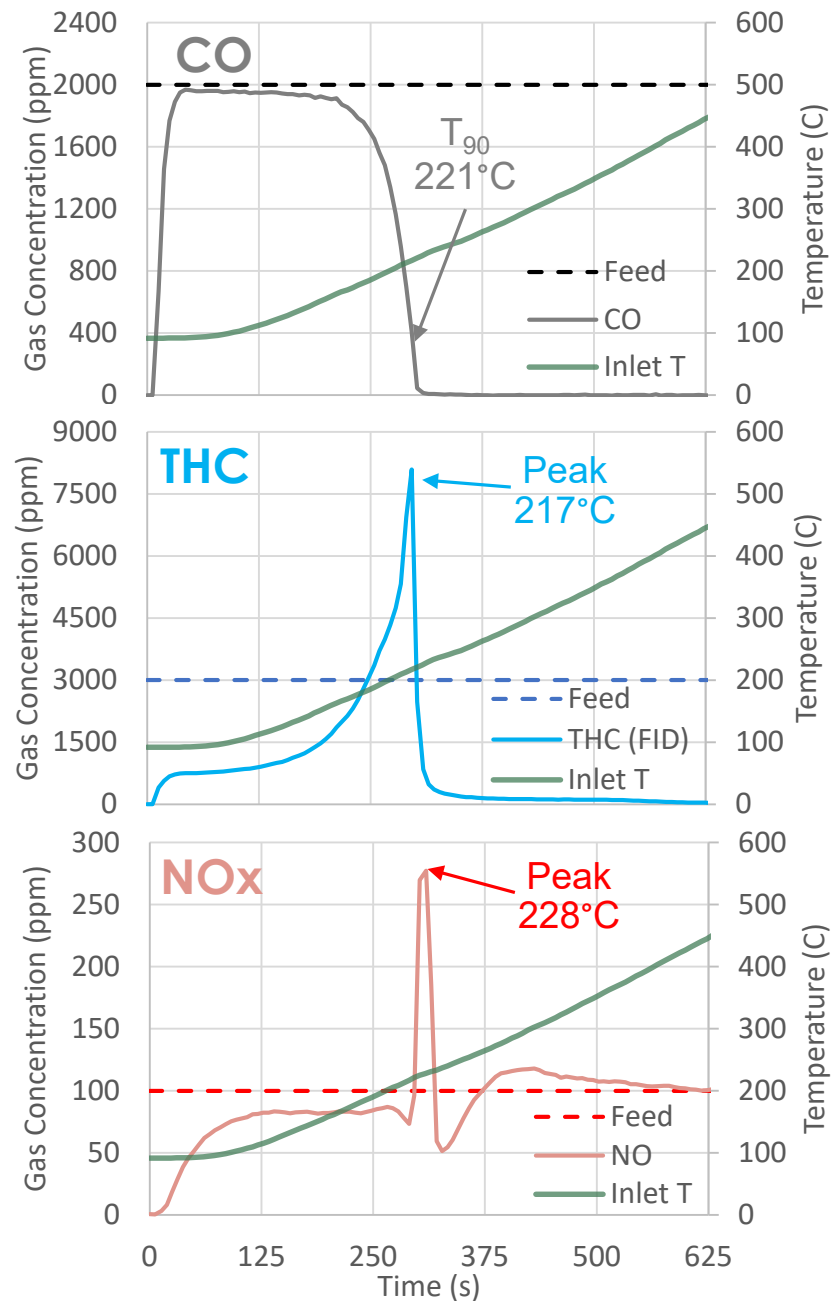
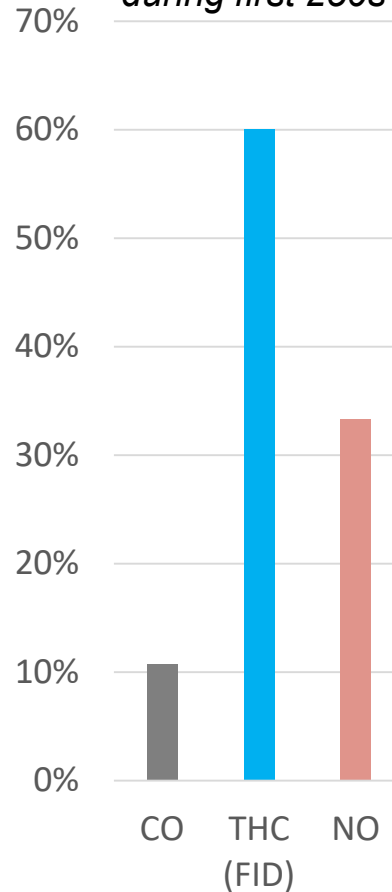
# Aging 40h at 800°C mostly impacts NO storage; release temperature increases ~15°C

## • Evaluation:

- Introduce reactants and immediately begin ramp
  - 40°C/min ramp to 620°C
- Physical Mixture of
  - 100 mg ZSM-5
  - 100 mg 1% Pd/CHA
  - 100 mg 0.9% Pt/0.5% Pd/SiO<sub>2</sub>@ZrO<sub>2</sub>
- Overall 133 L/g-h including all three catalysts (666 sccm)
- Higher percentage of HCs removed on aged sample
- NO uptake decreases
  - NO:Pt at 250s = 0.38
  - Based on mols in Pd/SSZ-13

HT-Aged 40h/800°C

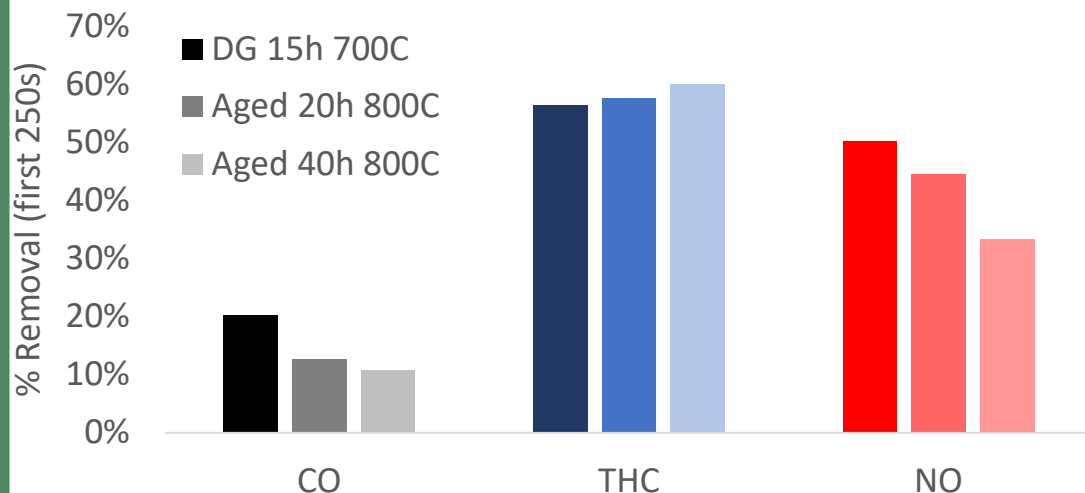
Overall %removal during first 250s\*



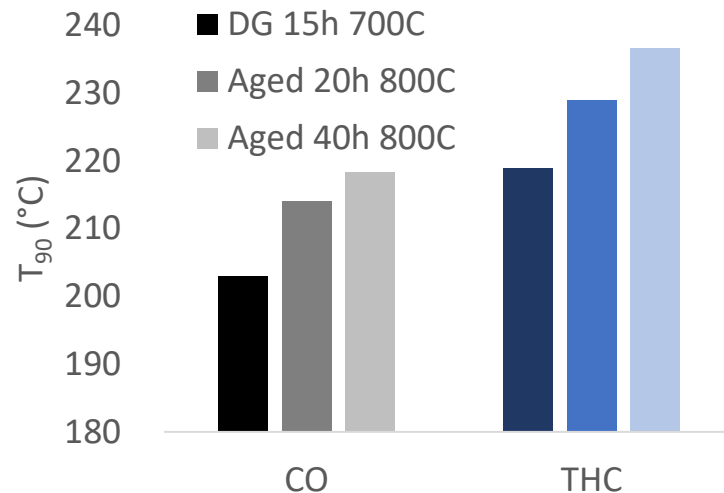
\* - Based on Ford study relevant to cold start and time to catalyst lightoff (SAE 2018-01-0938).

# Aging 3-component system generally impacts CO and NO functionality more than HC

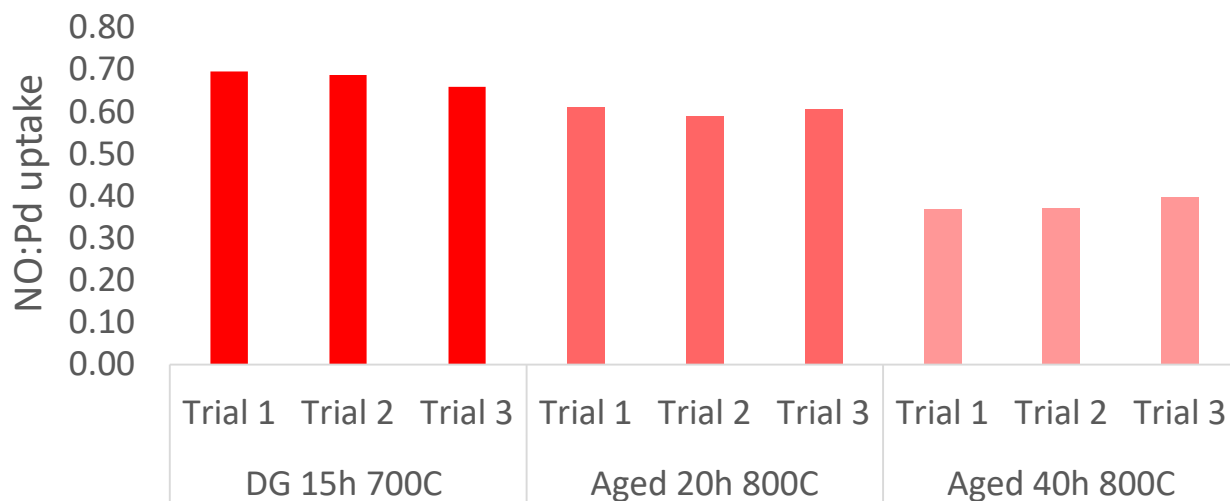
- The percentage removal of CO and NO decreases with aging, but not HC



- Reactivity decreases for both CO and HC



- Unlike in single component system the NO uptake is not decreasing from trial to trial
  - However, thermal aging impacts uptake



# Remaining Challenges

- Oxidation Catalysts**

*Need improved oxidation of HCs after aging*

- Passive NOx Adsorbers**

*NOx uptake is not fast enough*

*PGM utilization needs improvement under realistic conditions*

- Hydrocarbon traps**

*Increased storage capacity of lighter HCs will be necessary*

# Future Directions

Evaluate supports that are already made with emphasis on ceria-based supports\*

More characterization to understand strong interaction between support and PGM

Interesting collaboration starting with Harvard University

Work with CLEERS to understand what is slowing down uptake and investigate other options

Introduce surface studies to understand what is limiting access or limiting Pd Ion exchange

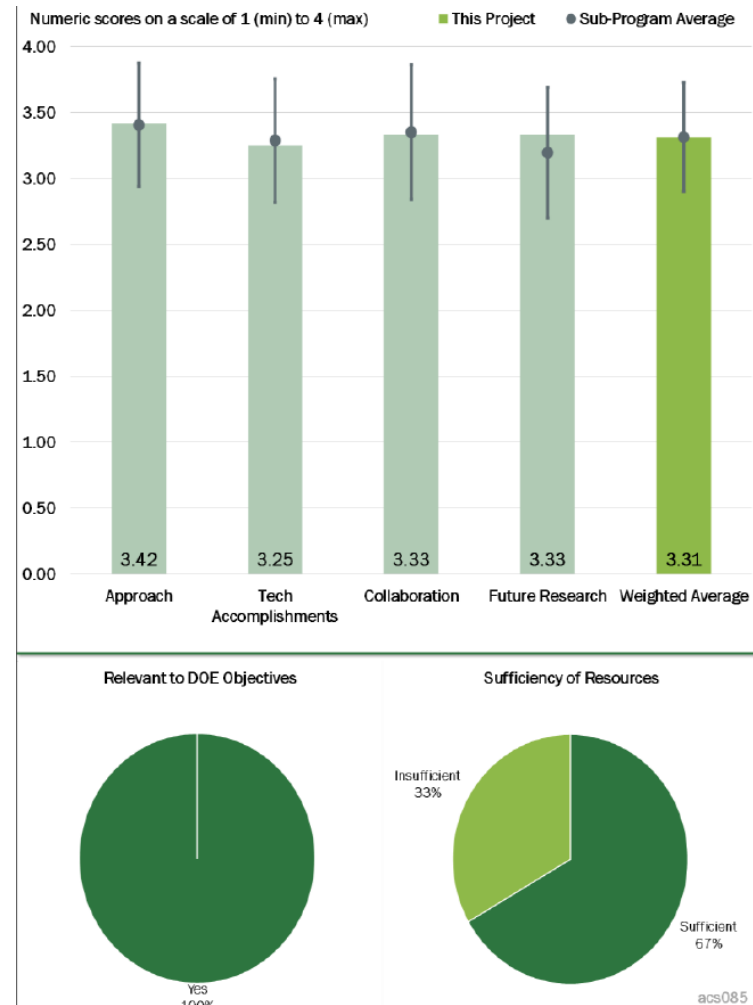
Investigate other zeolites or including non-PGM metals for ion-exchange

*Any proposed future work is subject to change based on funding levels*

\* - promising results recently published: Nie et al., Science 358, 1419–1423 (2017).

# Response to reviewer comments

- **REVIEWER: Implement severe aging earlier in the evaluation process**
  - Working to do this as much as possible, but also trying to understand where samples fail in case the aging conditions are not as severe as previously thought
- **REVIEWER: Better understanding of bi-metallics is needed and more characterization is warranted**
  - A specific goal of this years efforts and milestone highlights that; also hired post-doc with specific experience with bi-metallics
- **REVIEWER: Incorporate chabazite into the matrix of samples being evaluated**
  - Successfully procured CHA/SSZ-13 from commercial supplier and exchanged with Pd; large part of the results shown so far and will continue to be so



# Summary

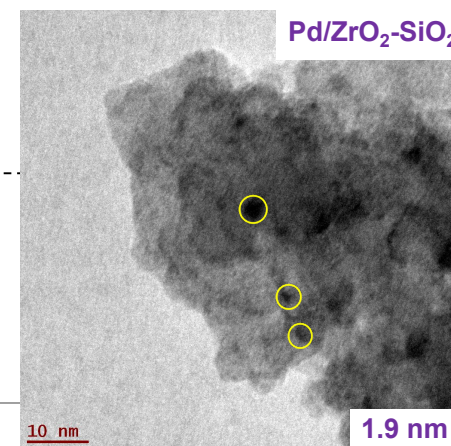
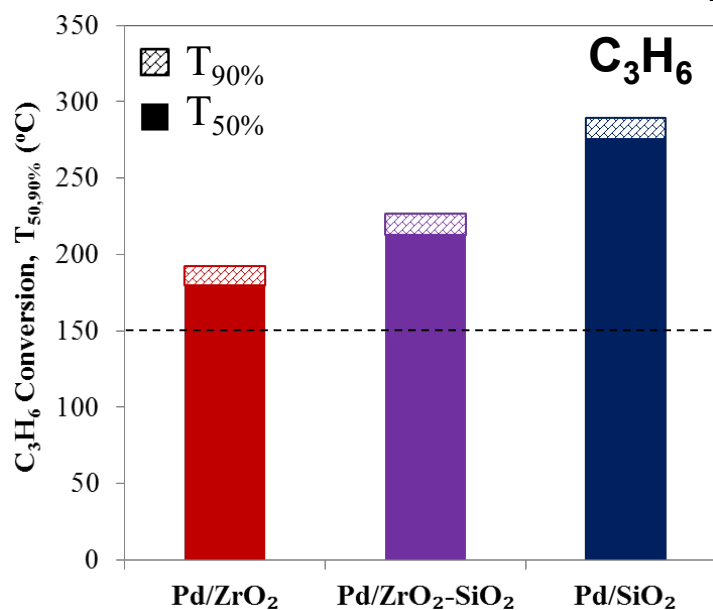
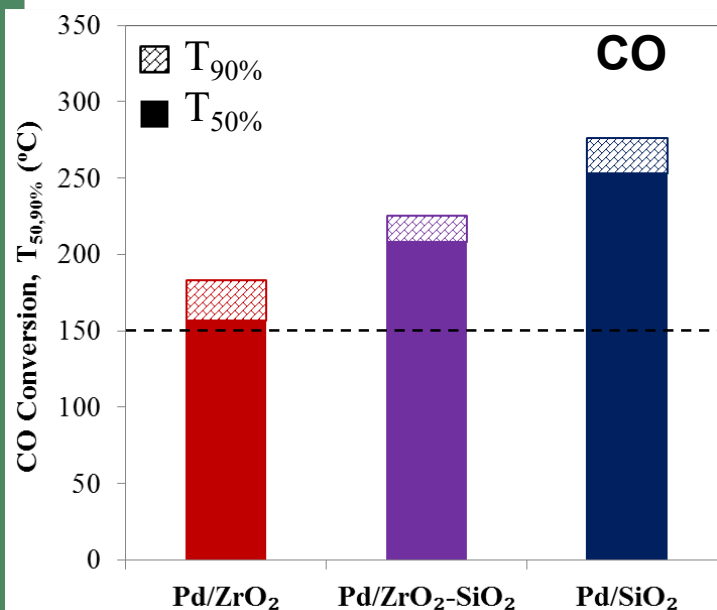
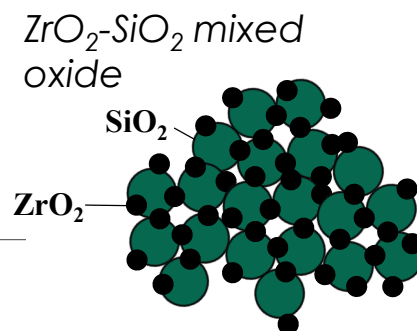
- **Relevance:** Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures ( $<150^{\circ}\text{C}$ ) to meet emission regulations
- **Approach:** employ low temperature protocols to evaluate novel catalysts and systems
- **Collaborations:** Wide-ranging collaboration with industry, academia, other DOE projects, & national labs maximizes breadth of study, guides research from other funding sources
- **Technical Accomplishments:**
  - Synthesized new class of novel supports to be investigated for improved durability and low temperature oxidation
  - Established new collaborations with University at Buffalo and Harvard University
  - Demonstrated HC trap functionality and durability of PGM-free zeolite
  - Evaluated Pd/SSZ-13 for passive NO<sub>x</sub> adsorption and discovered deactivation mechanism that occurs during evaluation as a single component
  - Demonstrated potential and durability of combining a non-PGM zeolite, Pd/SSZ-13 PNA, and oxidation catalyst to treat low temperature emissions
- **Future Work:**
  - Evaluation of new novel supports aiming to take advantage of the reported activity using ceria supports
  - New collaboration with Harvard investigating high surface area and stable material
  - Develop understanding of Pd ion-exchange with SSZ-13 and losses with evaluation
  - Investigate impact of non-PGM ion-exchanged metals on ZSM-5 and BEA for improved HC trap functionality, especially for smaller molecules



# Technical Backup Slides

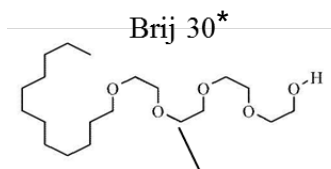
ZrO<sub>2</sub> support has shown excellent activity with Pd catalyst; but looking for improved activity and durability

- Pd/ZrO<sub>2</sub> has good activity, excellent thermal durability, good S tolerance
- Goal: further improve activity and sulfur tolerance
  - Support ZrO<sub>2</sub> on high surface area SiO<sub>2</sub>
- Initial effort not successful as Pd/ZrO<sub>2</sub> still more active
  - not a monolayer; 15% coverage of SiO<sub>2</sub> surface
  - Pd dispersed on both ZrO<sub>2</sub> and SiO<sub>2</sub>

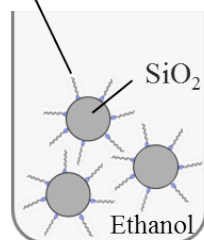
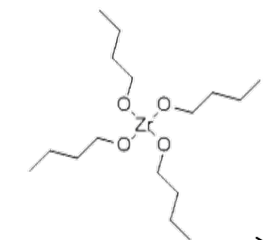


# New approach: Cover all of the $\text{SiO}_2$ surface with Zr

## **Synthesis of $\text{SiO}_2@\text{ZrO}_2$ core@shell Oxide Support**

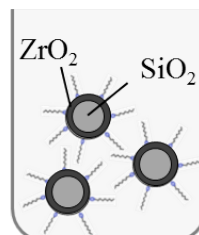


Zirconium Butoxide



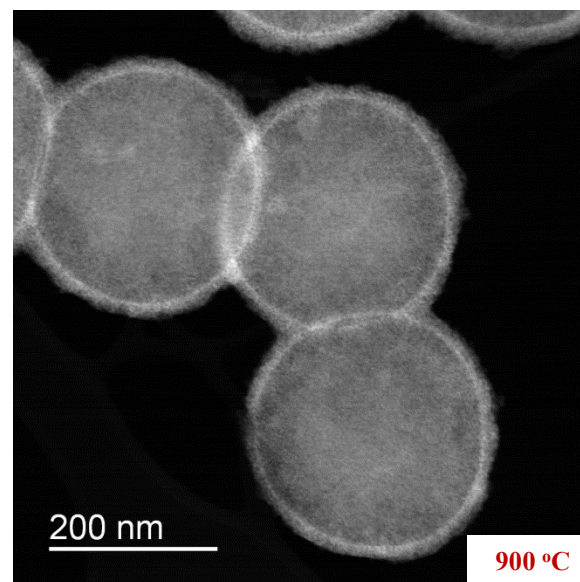
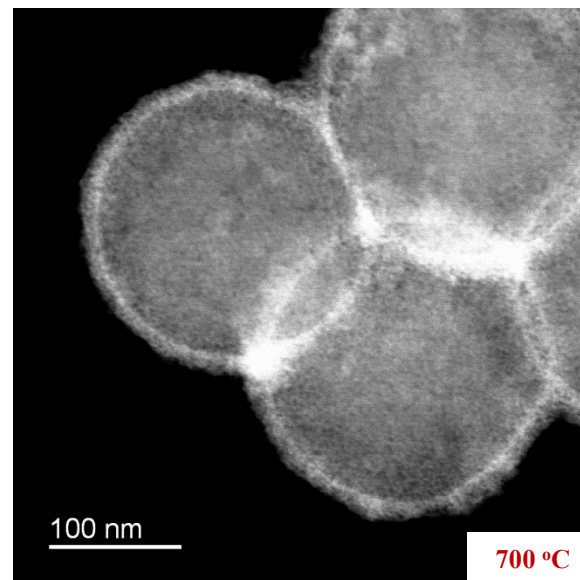
*Synthesis of silica spheres*

\*(Brij 30): Polyoxyethylene(4) lauryl ether

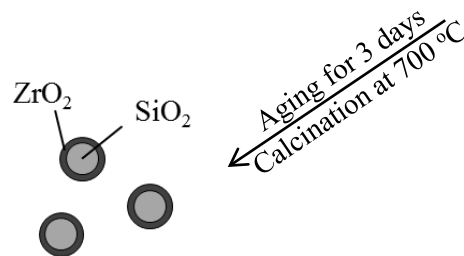


*Silica core and amorphous shell with zirconium hydroxide*

(8 w/w in butanol)



Material	Surface Area (m <sup>2</sup> /g)
ZrO <sub>2</sub>	97
ZrO <sub>2</sub> -SiO <sub>2</sub>	153
SiO <sub>2</sub> @ZrO <sub>2</sub>	210

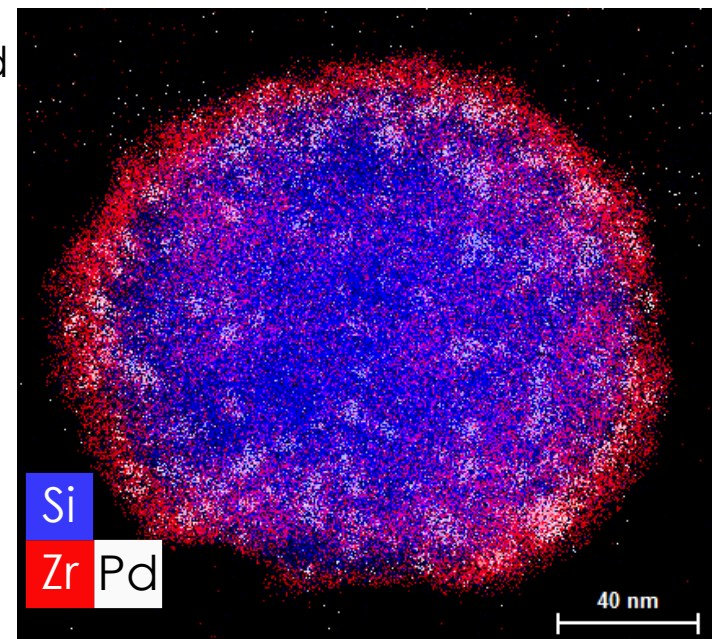
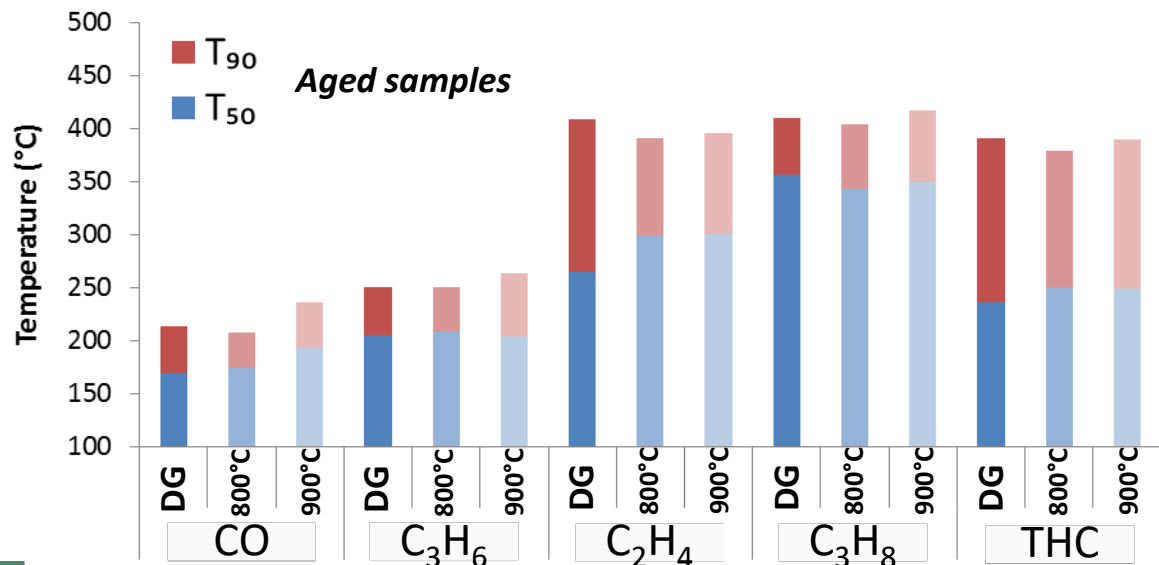
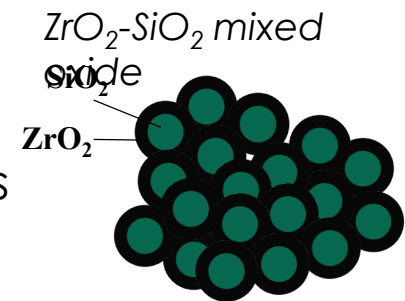


*Silica core and zirconium oxide shell after calcination at 700 °C*

- **SiO<sub>2</sub>** is located in the **core** and **ZrO<sub>2</sub>** in the **shell**
- The ZrO<sub>2</sub> **shell** seems to be **porous**
- Growth of SiO<sub>2</sub>@ZrO<sub>2</sub> spheres. Shell is maintained. Diameter at: **900 °C: ~250 nm**

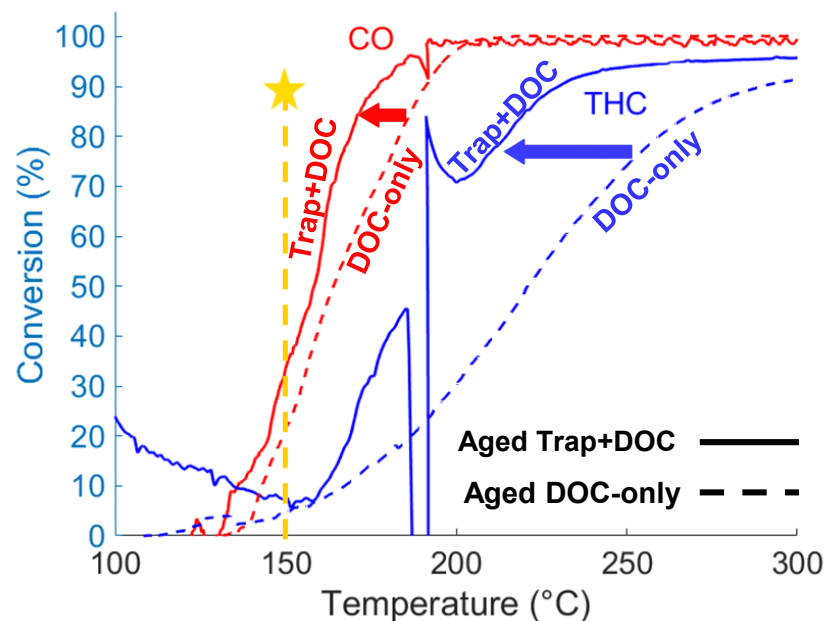
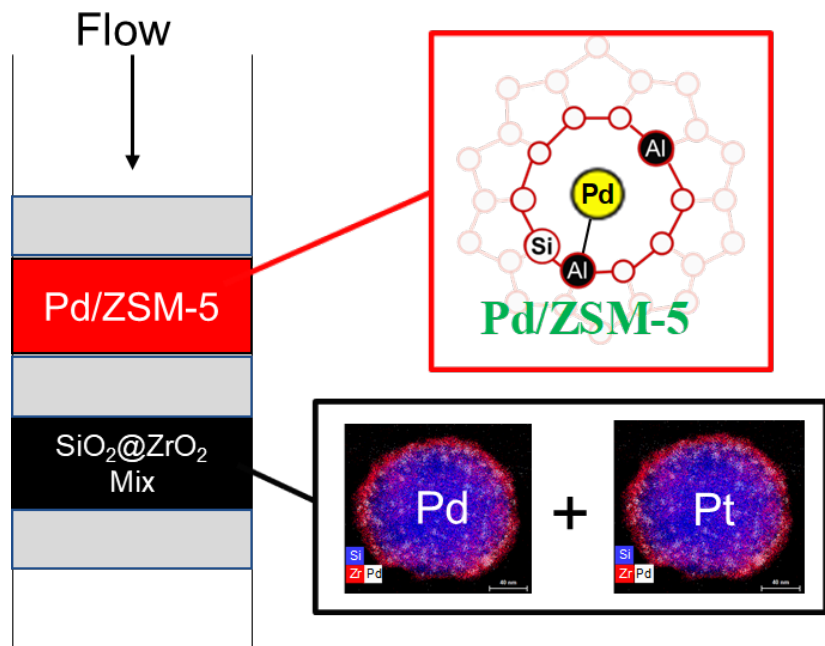
# New synthesis technique successfully creates durable $\text{ZrO}_2$ shell around $\text{SiO}_2$ core

- Able to synthesize a complete shell around  $\text{SiO}_2$  core using new technique  $\text{Pd}/\text{SiO}_2@\text{ZrO}_2$ 
  - Pd (1 wt%) deposition solely on  $\text{ZrO}_2$  outer shell
- While employing US-DRIVE low temperature protocols improved activity shown with this technique
- Robust after aging at  $900^\circ\text{C}$  for 10h
  - Improved initial dispersion technique still needed



This research was performed, in part, using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities.

# Trap materials + oxidation catalysts significantly improve overall system functionality after aging



Protocol aging: reaction conditions at 800°C for 50h, 5 ppm SO<sub>2</sub> @ 300°C 5 h  
Desulfation under cycling lean-rich conditions for 30 min at 500°C, 30s per condition

- Although Pd/ZSM-5 trap is heavily degraded, it still improves reactivity of system considerably in dual-bed configuration

*Conditions during 2°C ramp*

total HC<sub>1</sub>: 3000 ppm

C<sub>2</sub>H<sub>4</sub>: 500 ppm

C<sub>3</sub>H<sub>6</sub>: 300 ppm

C<sub>3</sub>H<sub>8</sub>: 100 ppm

C<sub>10</sub>H<sub>22</sub>: 2100 ppm

CO: 2000 ppm

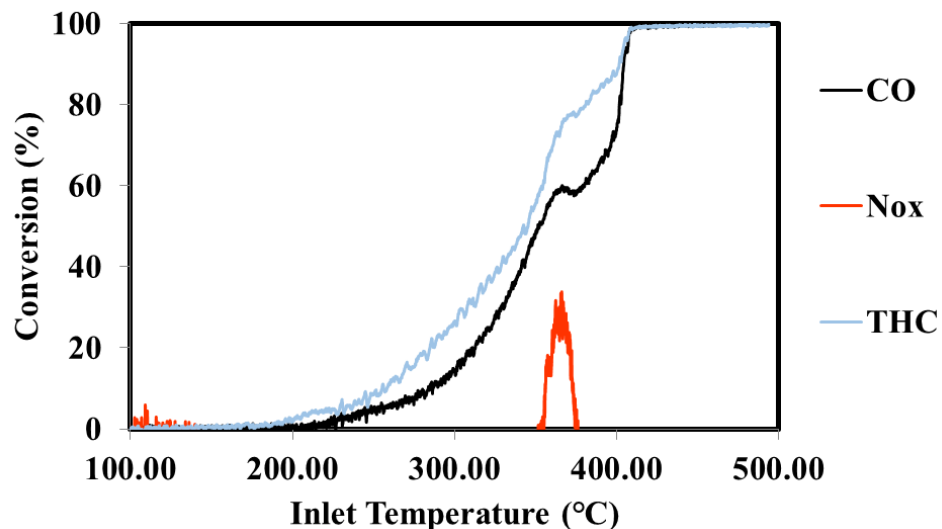
NO: 100 ppm

Also H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>

Pt/CeO<sub>2</sub> is also under consideration and showing remarkable PGM stability

- Simple incipient wetness technique
  - Calcined at 800°C
- Initial surface area is only 37 m<sup>2</sup>/g
- 1.4 nm size particles measured after aging
  - CO chemisorption
  - 750 °C in 10% H<sub>2</sub>O for 9h
- Significant room for improvement if dispersing CeO<sub>2</sub> on high surface area support

LTC-D-fresh sample-ramp up



LTC-D-aged sample-ramp up

